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I, CASSANDRA RICHARDS, ACTING TEAM LEADER EXAMINATION SUPPORT & SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PQ 3154 for a patent by CERAMIC FUEL CELLS LIMITED filed on 29 September 1999.

WITNESS my hand this
Tenth day of November 2000

CASSANDRA RICHARDS
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Regulation 3.2

CERAMIC FUEL CELLS LIMITED

AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"FUEL CELL ASSEMBLY"

The invention is described in the following statement:

FUEL CELL ASSEMBLY

The present invention relates to fuel cells and is particularly concerned with a tubular solid oxide fuel cell assembly.

Fuel cells convert gaseous fuels (such as hydrogen, natural gas, and gasified coal) directly into electricity via an electrochemical process. A fuel cell continuously produces power when supplied with fuel and oxidant, normally air or other oxygen-containing gas. A typical fuel cell consists of an electrolyte (ionic conductor, H^+,O^{2-}, CO_3^{2-}, etc.) in contact with two electrodes (mainly electronic conductors). On shorting the cell through an external load, fuel oxidises at the anode resulting in the release of electrons which flow through the external load and reduce oxygen at the cathode. The charge flow in the external circuit is balanced by ionic current flows within the electrolyte. At the cathode oxygen from the air or other oxidant is disassociated and converted to oxygen ions which migrate through the electrolyte membrane and react with the fuel at the anode/electrolyte interface. The voltage from a single cell under typical load conditions is in the vicinity of 0.6 to 1.0V DC and current densities in the range of 100 to 1000 $mAcm^{-2}$ can be achieved.

Several different types of fuel cells are under development. Amongst these, the solid oxide fuel cell (SOFC) is regarded as potentially the most efficient and versatile power generation system, in particular for dispersed power generation, with low pollution, high efficiency, high power density and fuel flexibility.

Numerous SOFC configurations are under development, including the planar, the tubular, the segmented and the monolithic designs. The planar or flat plate design has been widely investigated. In this concept, the components - electrolyte/electrode laminates and interconnect plates, which may have gas channels formed therein - are fabricated individually and then stacked together and sealed with a high temperature sealing material to form either a fixed or sliding seal.

SOFCs operate in the vicinity of 700 - 1000°C, and planar SOFCs are inherently difficult to seal, especially against thermal shock and cycling. Furthermore, because of the way planar SOFCs are stacked with interconnects or gas separators therebetween, the interconnects add mass and complexity of materials to the planar SOFC design.

Many of the disadvantages of planar SOFCs are alleviated in tubular SOFCs. In the tubular concept, one of the oxygen-containing gas and fuel gas is passed along the interior of the tube, while the other gas is passed over the exterior.

In designs proposed by Westinghouse, the oxygen-containing gas is suppled to the interior of the tubular fuel cell, so the cathode is on the inside, whereas in designs proposed by Mitsubishi the fuel gas is supplied to the interior of the tubular fuel cell, so the anode is on the inside. In both proposals, the fuel cell assemblies including the fuel cell and the current collectors on both the anode and cathode sides are formed of ceramic or cermet materials leading to a structure which is susceptible to the fragility of these inherently brittle materials. Additionally, these tubular current collectors have an inherently long electron flow path compared to those of other designs and, since the electronic conductivities of the anode and cathode materials are relatively low, resistive losses tend to be high. This feature has tended to limit the power densities of tubular fuel cells and/or has required relatively large structures to achieve the desired currents.

Furthermore, because of the relatively poor thermal conductivity of ceramic materials, thermal or power variations within a tubular fuel cell formed primarily of ceramic materials, or within a bundle of such tubes, can cause relatively high localised temperature gradients which in turn introduce high localised strains into the tube(s). These can lead to the fracture of the tube(s).

It is an object of the present invention to alleviate the disadvantages of the prior art.

According to a first aspect of the present invention there is provided a tubular fuel cell assembly including a fuel cell having an anode side defining a passage for fuel gas, the anode

side comprising an anode layer and an anode-side current collector in electrical contact with the anode layer, a solid oxide electrolyte layer on a radially outer surface of the anode layer, a cathode layer on a radially outer surface of the electrolyte layer, and a cathode-side current collector on the radially outer surface of the cathode layer of the fuel cell, wherein the anode side current collector comprises a metallic structure which is adapted to permit fuel gas in the passage to contact the anode layer and wherein at least the surface of the metallic structure is formed of Ni or Ni alloy.

By the first aspect of the present invention, the current collection on the anode side of the fuel cell is substantially improved over nickel cermet current collectors, with an electrical conductivity about 500 times greater at the operating temperature of an SOFC, about 800 to 1000°C, and a greatly improved thermal conductivity. This permits substantially smaller devices to be adopted and losses to be reduced. Additionally, the metallic structure of the anode side current collector may provide a degree of reinforcement to the SOFC, also permitting smaller devices to be adopted while at the same time improving thermal and mechanical shock resistance. This may allow the fuel cells to be employed in smaller and possibly even mobile applications.

The overall diameter of the tubular fuel cell assembly may be in the range 2 to 20mm or larger, preferably 3 to 10mm. A plurality of the tubular fuel cell assemblies may be disposed side by side or bundled together and electrically connected in parallel or in series. The tubular fuel cell assemblies should be slightly spaced from each other to permit oxygen-containing gas, preferably air, to flow over the cathode layers, but each tubular fuel cell assembly may be mechanically connected to one or more adjacent tubular fuel cell assemblies to enhance the shock resistance of the overall fuel cell bundle. Thus, in one embodiment the plurality of tubular fuel cell assemblies may be connected in effectively a honeycomb structure. The mechanical connections may be continuous along the length of the tubes, but are preferably intermittent and may also provide electrical interconnection between the assemblies. Each tubular fuel cell assembly may have any desired length, for example in the range about 90 to 1000mm, preferably 200 to 300 mm.

The anode side current collector may take any of a variety of forms, or a combination of two or more of these forms, and may have a thickness in the range of about 20 to 200μm or greater depending upon the configuration and, for example, the desired current density.

In one embodiment, the anode side current collector may comprise a spiral or mesh of nickel thread which preferably extends the full length and periphery of the passage. Thus, preferably the overall shape of the anode side current collector corresponds to that of the passage, and is most preferably tubular. Such a spiral or mesh anode side current collector may provide a degree of reinforcement to the fuel cell, especially if it is embedded in the anode layer.

Alternatively or in addition, the anode-side current collector may comprise an internal support structure, such as a support tube, formed of or coated with nickel or nickel alloy. The internal support structure must permit free flow of fuel gas to the anode layer and thus it may comprise an expanded or woven mesh or otherwise perforated tube of nickel or nickel alloy. Instead, the support tube may be formed of a porous nickel material. Alternatively, the support tube may comprise a nickel or nickel alloy coated material, with the substrate material comprising, for example, a heat resistant metal acting as the primary heat conductor for each tubular fuel cell assembly. The substrate may be an expanded or woven mesh or otherwise perforated tube with perforated nickel or nickel alloy foil wrapped over the sheet, or with nickel or nickel alloy deposited or otherwise coated onto it. Several construction variations are possible, for example Ni mesh on steel mesh, Ni plated mesh on Ni plated steel mesh, centrifugally cast Ni spiral on Ni plated steel mesh or perforated Ni sheet wrapping on plain steel mesh, with the steel optionally being replaced by another thermally conductive material with adequate high temperature properties. As noted above, the nickel or nickel alloy layer may have a thickness in the range of about 20 - 200μm.

To allow for the differential expansion of the aforementioned internal support structure during thermal cycling of the tubular fuel cell assembly, and for ease of assembly, the support structure may be a loose fit in the passage of the tubular fuel cell assembly at least at room temperature and expand into mechanical and electrical contact with the anode layer and/or other anode-side current collector at the operating temperature of the fuel cell assembly.

An advantage of combining the aforementioned spiral or mesh thread current collector with the internal support structure is that the support structure may provide optimum electrical and thermal conductivity as well as mechanical shock resistance, while the thread current collector may be much finer in scale and provide more effective electron collection. The thread may be wound or otherwise provided on the support structure.

As an alternative to, or in addition to, a support tube which acts as a heat conductor as well as an electrical conductor, a separate tube liner may be used within the passage of the fuel cell assembly to act as a superior thermal conductor, for example of copper. The tube liner may itself be tubular or have any other suitable cross-section. A copper tube liner may have those surfaces exposed to the nickel on the anode side of the fuel cell protected with, for example, alumina to prevent poisoning of the nickel when the nickel is to be used as a catalyst for steam reforming of methane fuel gas supplied to the passage.

The anode layer is preferably a nickel cermet, for example Ni/ZrO_2, but other ceramic-type materials may be contemplated. The anode layer is preferably relatively thin with a thickness in the range of about 50 to 500 μm, for example about 200 μm. The anode layer is a porous layer which may be formed by any of a variety of suitable tube forming methods, such as extrusion or drawing. Preferably the anode layer is extruded and may conveniently be extruded onto a previously-formed tube of the anode side current collector which becomes at least partly embedded in the anode layer. The extrusion may be performed hot, warm or cold, and the preferred cermet material is subsequently dried and/or sintered. This may be assisted by microwave heating.

The solid oxide electrolyte layer is preferably a Y_2O_3 - doped ZrO_2, for example 8YSZ. Preferably the solid oxide electrolyte layer is relatively thin with a thickness less than 70 μm, for example about 20μm or less. The electrolyte is preferably continuous along the full length and around the circumference of the tubular anode layer and may be formed in any of a variety of ways bearing in mind that the electrolyte layer must be a dense, defect-free layer to prevent mixing of the fuel gas and oxygen-containing gas through the fuel cell. The electrolyte material may be deposited onto the tube by, for example, slurry coating. Other

possible methods include extrusion onto the anode layer or co-extrusion with it, sol gel spin casting and electrophoretic coating.

A variety of different materials are known for use as the cathode layer of a solid oxide fuel cell, but the currently preferred materials are perovskites such as strontium doped lanthanum manganite (LSM) and/or strontium doped praseodymium manganite (PSM) or La cobaltites, preferably having a total thickness in the range of about 30 to 100 μm.

In a preferred embodiment, the cathode layer is discontinuous along the tubular fuel cell assembly and/or around it. This effectively provides a plurality of adjacent fuel cells in the tubular fuel cell assembly, albeit with a common anode layer and a common solid oxide electrolyte layer. In one embodiment, the individual portions of the cathode layer are separated longitudinally by a gap in the range of about 2 to 10 mm about every 25 to 80 mm, most preferably about every 40 to 50 mm. Likewise, the cathode layer may have one or more similar gaps extending axially along the tube, preferably with two diagonally opposed gaps. The individual portions of the preferred divided cathode layer may be electrically connected with adjacent portions along and/or around the tube and/or with adjacent tubes in a fuel cell bundle.

The cathode side current collector preferably comprises a metallic material having a relatively high electrical conductivity. Such a metallic current collector may comprise a mesh which is advantageously screen printed or otherwise deposited on the cathode layer or each portion of the preferred divided cathode layer. Such a mesh may have a thickness in the range of about 20 to 100μm. Where the cathode layer is divided longitudinally to form plural fuel cells along the tube, one or more electrically conductive metallic strips, which may be of the same material as the mesh, may extend the length of the tubular fuel cell assembly, or part of it, and be screen printed or otherwise deposited on the cathode layer. If a metallic strip bridges two or more of the plural fuel cells it may electrically connect them in series. Alternatively, or in addition, the individual fuel cells may be connected by other means in series or in parallel, that is with adjacent fuel cell assemblies. The aforementioned meshes may be deposited over the metallic strip or strips or at least one of the metallic strips, or be otherwise

electrically connected thereto. The or each metallic strip could be disposed on the electrolyte layer in a respective longitudinal gap in the cathode layer in which case it may have a width less than the longitudinal gap. The or each metallic strip may have a thickness in the range of about 100 to 200μm, preferably about 100 μm. Preferably, the metallic mesh and/or strip is formed in silver, but other noble metals, such as platinum, or their alloys would be suitable.

According to a second aspect of the present invention there is provided a tubular fuel cell assembly including a fuel cell having an anode side defining a passage for fuel gas, the anode side comprising an anode layer and an anode-side current collector in electrical contact with the anode layer, a solid oxide electrolyte layer on a radially outer surface of the anode layer, a cathode layer on a radially outer surface of the electrolyte layer, and a cathode side current collector on the radially outer surface of the cathode layer of the fuel cell, wherein the cathode side current collector comprises a metallic layer of noble metal or noble metal alloy which is adapted to permit oxygen containing gas around the fuel cell to contact the cathode layer. Preferably, the noble metal is silver.

By the second aspect of the present invention, the current collection on the cathode side of the fuel cell is substantially improved over the known ceramic-based current collectors, with an electrical conductivity of about 4 x 10^5 S/cm for silver being $>$ 10,000 times higher at the operating temperature of an SOFC. This permits substantially smaller structures to be adopted. Additionally, the noble metal or alloy current collector may provide a degree of reinforcement to the SOFC, also permitting smaller structures to be adopted while at the same time improving shock resistance.

The shock resistance of the tubular fuel cell assembly in accordance with the second aspect of the present invention may be greatly enhanced by welding or otherwise joining a plurality of the tubular fuel cell assemblies together in a bundle, for example in a honeycomb structure. Advantageously this may be done using the same material as the material of the cathode side current collector, so that the connector means may provide an electrical flow path between adjacent assemblies. Thus, also according to the second aspect of the present invention there

is provided a fuel cell bundle comprising a plurality of tubular fuel cell assemblies each in accordance with the second aspect of the invention each connected to at least one other tubular fuel cell assembly by connector means formed of the material of the cathode side current collector.

Preferably, the cathode side of the tubular fuel cell assembly in accordance with the second aspect of the invention has one or more of the features described above of the cathode side of the tubular fuel cell assembly in accordance with the first aspect of other invention.

The anode side current collector of the tubular fuel cell assembly in accordance with the second aspect of the present invention may comprise a nickel cermet as is known from the prior art, but preferably is in accordance with the first aspect of the present invention, optionally with any of the preferred features associated therewith which for convenience only will not be described again.

Similarly, the anode layer, solid oxide electrolyte layer, cathode layer and other features of the tubular fuel cell assembly in accordance with the second aspect of the present invention are each preferably as described in accordance with the first aspect of the present invention, optionally with any of the preferred features associated therewith, and for convenience only will not be described again.

One embodiment of a tubular fuel cell assembly in accordance with the present invention will now be described by way of example only with reference to the accompanying drawings in which:

Figure 1 is a cross-section through one embodiment of a single tubular fuel cell assembly;
Figure 2 is a perspective view of a bundle of 18 of the tubular fuel cell assemblies of Figure 1, each fuel cell assembly having plural fuel cells, the fuel cells in some of the assemblies being connected in series, but in others not, as shown in Figure 3;
Figures 3a and 3b together are a plan view of the bundle of Figure 2, partially cut away and not to scale, showing in Figure 3a the series connection of the aligned cells in each assembly

and in Figure 3b the lack of series connection; and

Figures 4a and 4b together are a schematic end view of a bundle of 18 of the tubular fuel cell assemblies of Figure 1 showing two alternative means for linking adjacent fuel cell assemblies in parallel.

Referring to Figure 1 of the drawings there is shown in cross-section (not to scale) a tubular fuel cell assembly 10 comprising a porous Ni ZrO_2 cermet anode layer 12 defining a tubular passage 14 for fuel gas at the inner surface of the fuel cell assembly. A mesh 16 of nickel strands is in electrical contact with the anode layer 12, and optionally at least partly embedded in it. The mesh has a thickness of about 50μm and the spacing between strands is 1-2mm. The nickel mesh 16 is connected to electrical connectors (not shown) and acts as a current collector on the anode side. The nickel mesh 16 may be preformed and the porous anode layer 12 may be extruded onto it and/or around it.

The anode layer 12 may have a thickness of about 200 μm, and a dense 8YSZ solid oxide electrolyte layer 18 having a thickness of about 20 μm is disposed continuously over the anode layer 12. The electrolyte layer 18 may be co-extruded with the anode layer or, for example, first formed by casting and rolling into a green tape which is spirally wound onto the tubular anode layer and cured.

A porous cathode layer 20, for example of or incorporating LSM, having a thickness of about 50 μm is disposed on the electrolyte layer 18.

The cathode layer 20 is discontinuous around the circumference of the tubular fuel cell assembly 10, with two diagonally opposed longitudinal gaps 22 defining the discontinuity. In addition, although not shown in Figures 1 and 4, the cathode layer 20 is divided longitudinally by circumferential gaps 23 such as shown in Figures 2 and 3. As with the gaps 22, the circumferential gaps 23 extend through to the electrolyte layer 18 to effectively provide a series of individual fuel cells with common electrolyte and anode layers 18 and 12 as well as a common anode side current collector 16. The overall diameter of the tubular fuel cell assembly 10 may be 10 mm and the gaps 22 and 23 between adjacent portions of the cathode

layer 20 may be about 4 mm in width, but smaller and larger versions are possible.

A respective mesh 24 of silver is disposed over each portion of the cathode layer 20, each of which may be screen printed onto the cathode layer portion. The silver meshes 24 disposed over each circumferentially spaced longitudinal array of cathode layer portions may be electrically connected to each other by a respective longitudinal strip 26 of silver which may be screen printed onto the cathode layer 20 adjacent a respective one of the longitudinal gaps 22 between the cathode layer portions. Each strip 26 has a width of about 3 mm and a thickness of about 100μmm. Thus, in this embodiment, the circumferentially adjacent silver meshes 24 are not connected directly, but the longitudinally adjacent silver meshes 24 are connected by the silver strips 26. Alternatively, a respective silver strip 26 is provided for each cathode layer portion. The silver strips may be regularly connected to electrical connectors (not shown) to allow for current collection when fuel gas such as moist hydrogen is passed through the tubular passage 14 and oxygen-containing gas such as air is passed over the cathode layer 20 at the SOFC operating temperature of 700 to 1000°C.

Figures 2 and 3 show a bundle 38 of 18 tubular fuel cell assemblies 10 in six columns of three. Each assembly 10 in Figure 3a has two longitudinal series of silver strips 26 with each silver strip 26 associated with a respective cathode layer portion and fuel cell. Such an arrangement is also shown in Figure 2, although, for convenience only, the silver strips 26 have only been shown in the foremost column of three assemblies 10.

As shown clearly in the alternative embodiment of Figure 3b, the four fuel cells separated by three circumferential gaps 23 in the cathode layer 20 and the silver mesh 24 in each fuel cell assembly 10 are connected in series by the diagonally opposed longitudinally extending silver strips 26 disposed, in this case, over the mesh 24.

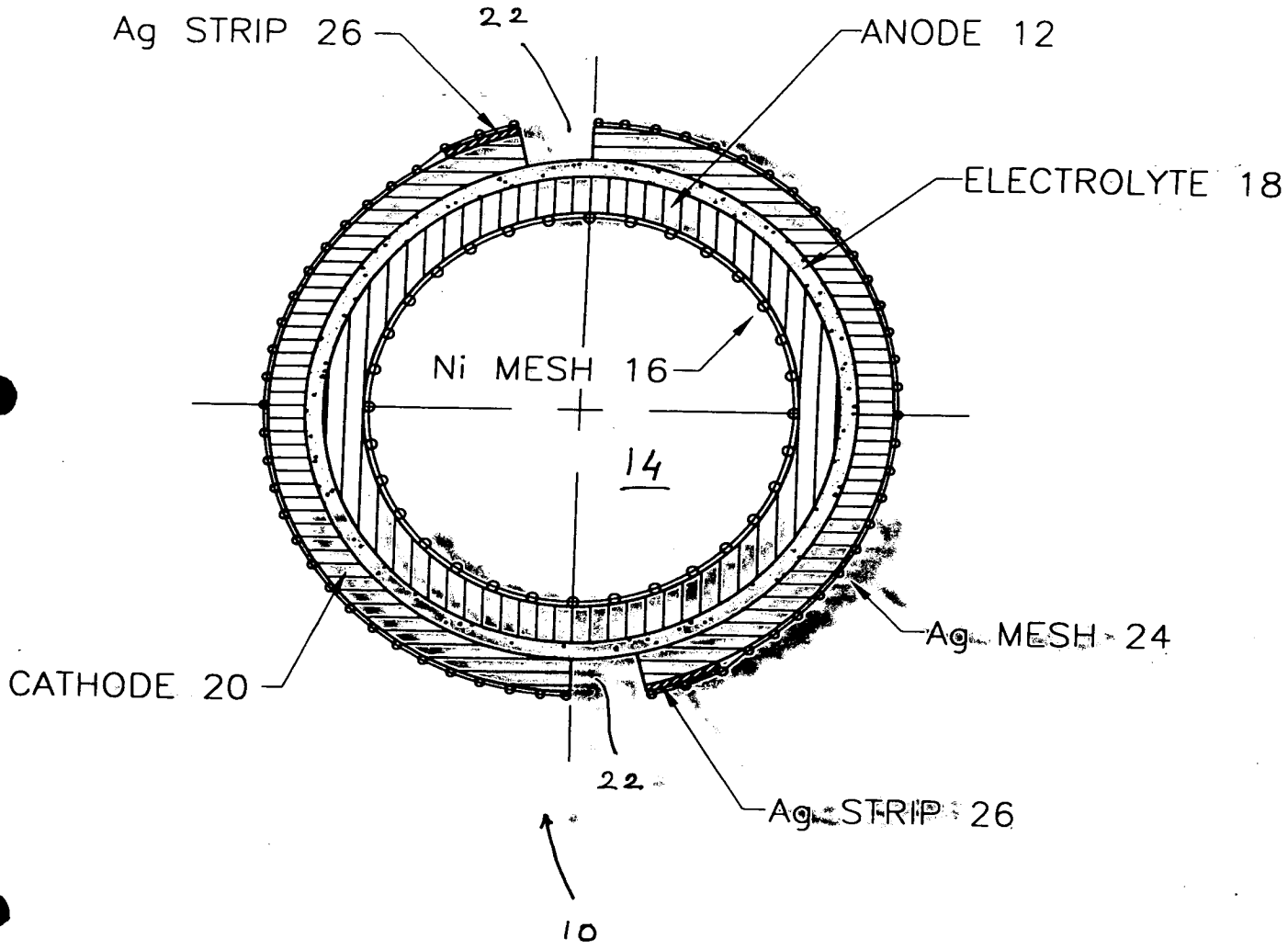
Two or more of the assemblies 10 in Figures 2 and 3 may be mechanically supported and/or electrically connected at one or both ends and/or between the ends, for example as described with reference to Figure 4, but are shown physically spaced from each other and without support or connections for clarity.

Referring now to Figure 4, two optional methods of mechanically and electrically connecting adjacent assemblies 10 in bundles each comprising three rows of three assemblies are shown in Figures 4a and b, respectively. In Figure 4a, the assemblies 10 in each row are shown connected in parallel, while in Figure 4b the assemblies 10 in each column are shown connected in parallel. In both arrangements, the connectors are formed of silver welded to the interrupted silver strips 26 of Figure 3a, but in Figure 4a they are illustrated as intermittent solid blocks 27 to provide a mechanically rigid link while in Figure 4b they are illustrated as intermittent hollow and flexible connectors 28 to better tolerate variations in shape and size of the assemblies 10. It will be appreciated that either type of connector 27 and 28 may be used to connect the rows and/or columns of tubular fuel cell assemblies and that the assemblies 10 may also be connected at one or both ends.

The solid blocks 27 or hollow connectors 28 may additionally or only connect adjacent fuel cells in each fuel cell assembly 10 in Figure 3a in series, but in Figure 4 each cell in each tubular assembly 10 is connected not to the adjacent cell on the same assembly 10, but to the nearest neighbour in the next column or row of tubular assemblies 10, ie. only in parallel.

While the tubular fuel cells described herein are of circular cross-section, this is not essential and they may be of any suitable cross-section. The terms "tubular" and "tube" as used herein shall be construed accordingly.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope.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Ni MESH 16
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FIG. 1

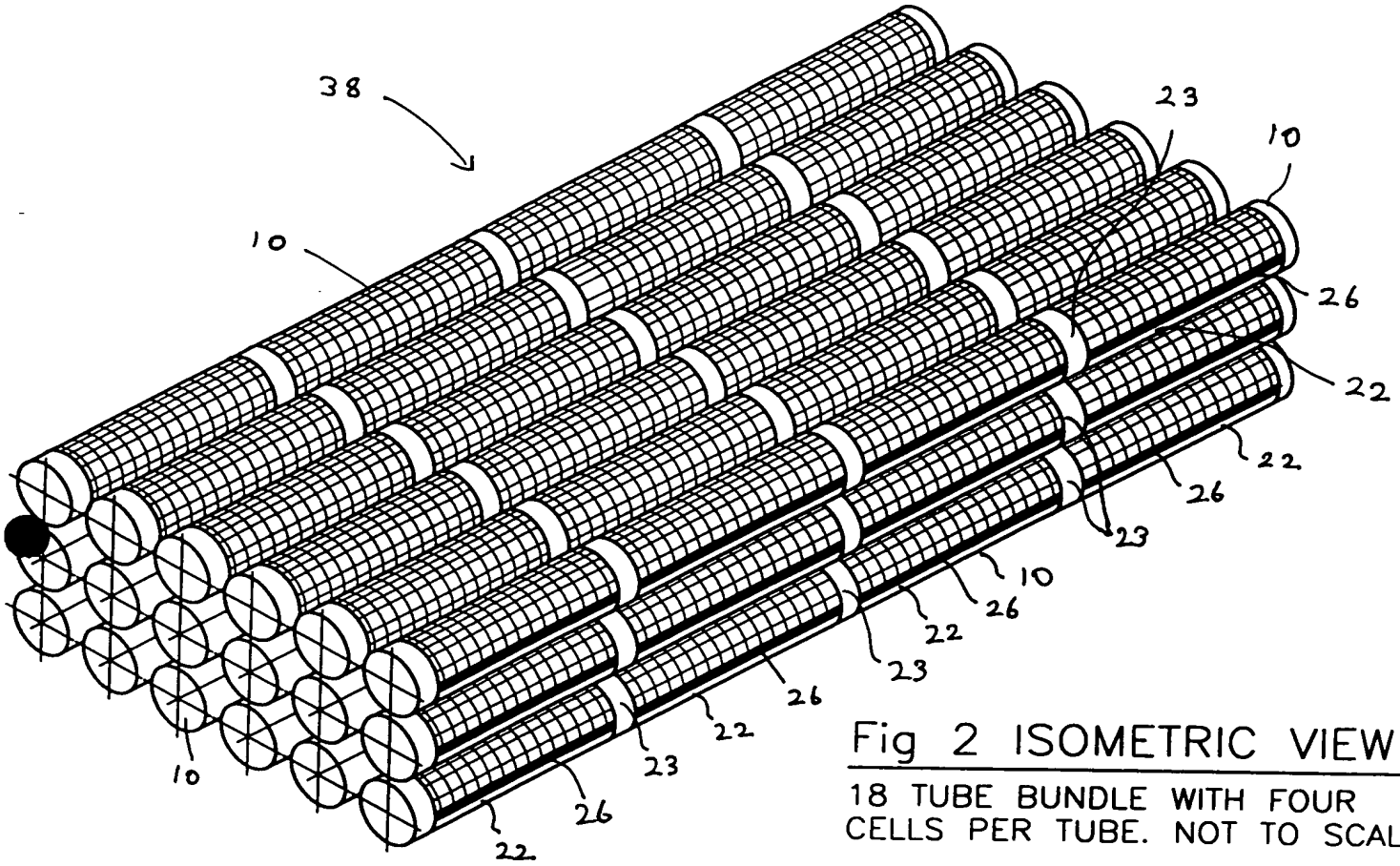

Fig 2 ISOMETRIC VIEW

18 TUBE BUNDLE WITH FOUR CELLS PER TUBE. NOT TO SCALE

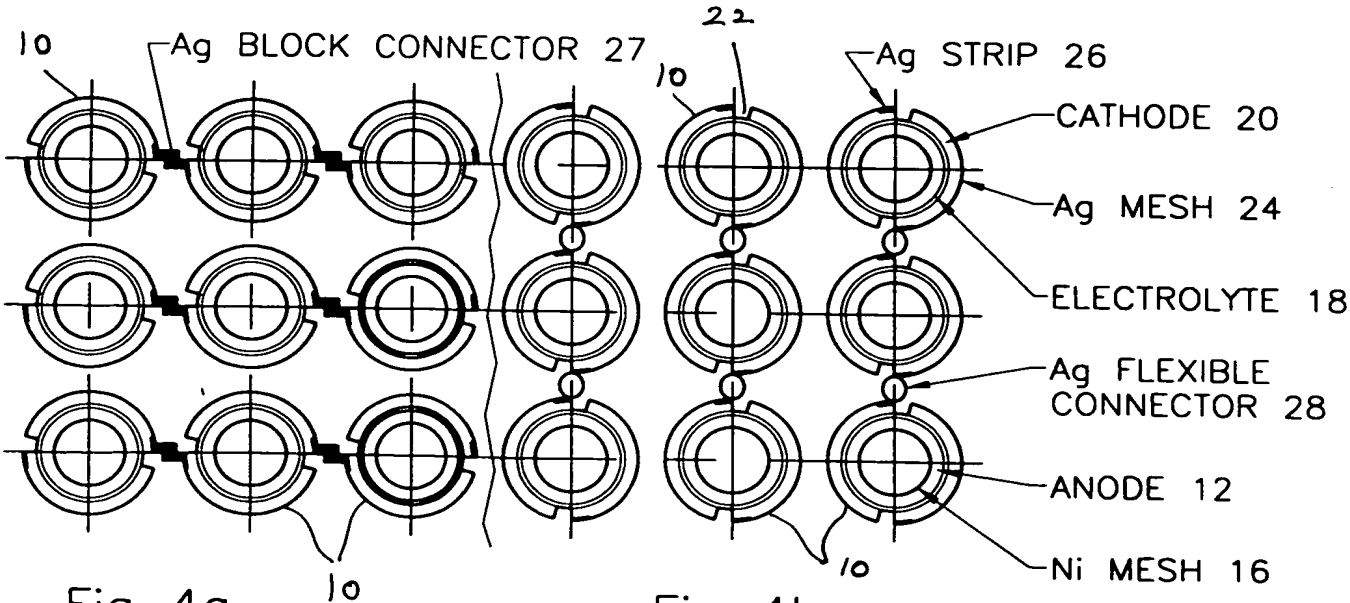

Fig 4a

Fig 4b

END ELEVATION

FIG. 3b

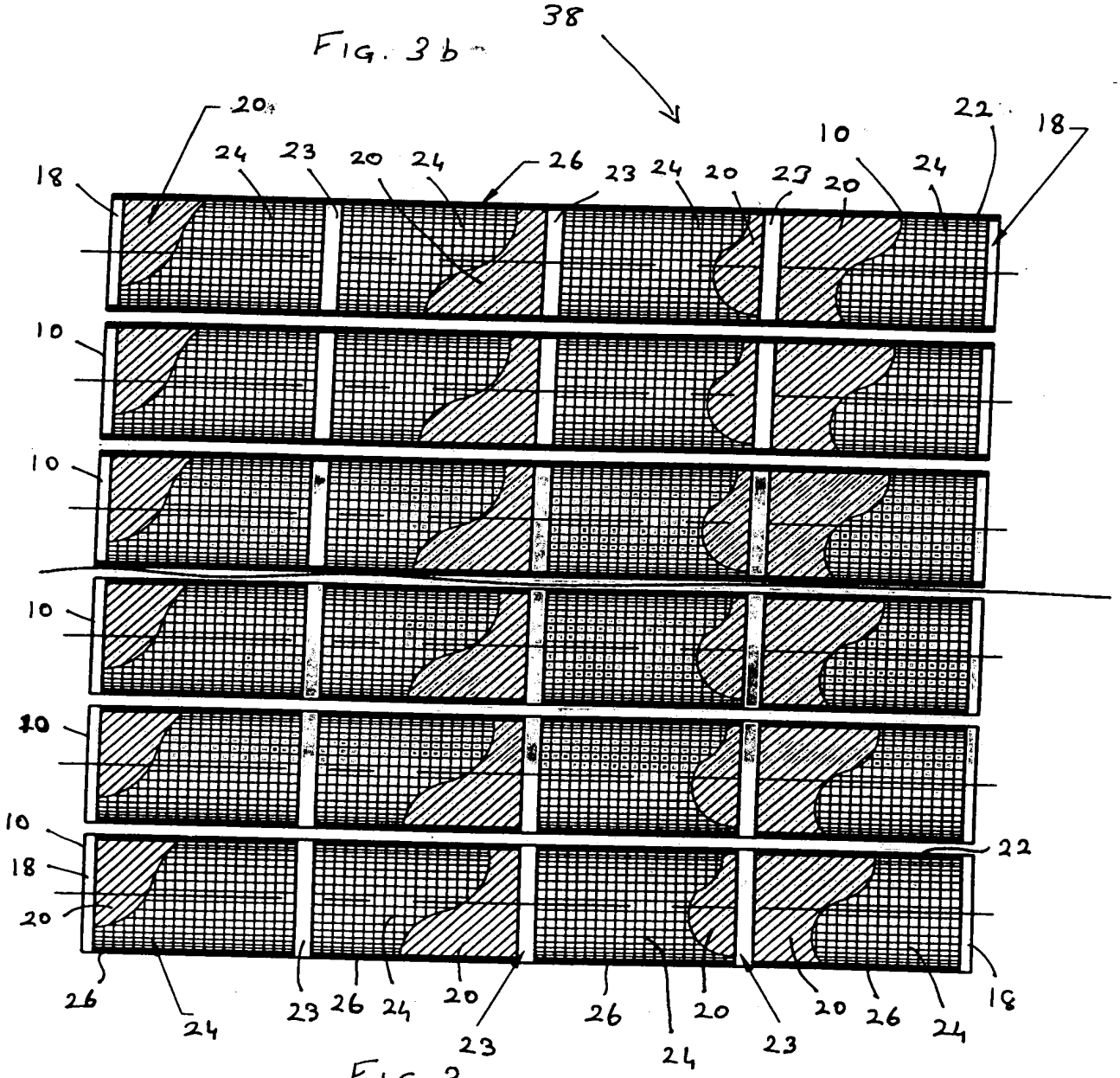
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FIG 3a